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COATINGS. ENAMELS

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TINTED LOW-MELTING ENAMELS FOR ALUMINUM

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The possibility of formation of low-melting glasses in the $R_2O – RO – Al_2O_3 – B_2O_3 – TiO_2 – P_2O_5$ system at a firing temperature of 550°C is investigated. A correlation of glass formation in the considered system with the content of Al_2O_3 and P_2O_5 is established, and the composition of a transition layer with crystalline phases of $Na_2O \cdot P_2O_5$, Al_2O_3 and $Al_2O_3 \cdot P_2O_5$ is determined.

Enameling of metals, especially nonferrous lightweight ones, is becoming topical due to progress in construction and the improving economy. Owing to such properties as low density, good workability, high impact strength, and good corrosion resistance, aluminum has become widespread as a structural material in engineering, construction, and production of consumer articles. Glass matrices that used to be typical in production of enameled aluminum articles often contained lead oxide, had insufficient chemical resistance, a limited color range, and fused at 600°C, which is undesirable for low-melting aluminum.

However, enameling of aluminum is a labor-consuming process, since in the synthesis of coatings one should take into account the high TCLE of enamel, equal to $252 \times 10^{-7}\ K^{-1}$ and its low melting point, equal to 658°C. Therefore, in designing enamels, it is necessary to take into account that enamels should have a low melting point ensured not by lead oxides but by some other fluxes, have a TCLE close to the TCLE of metals, and have good ornamental properties. In view of the presence of a great quantity of alkaline components, enamels should have satisfactory chemical resistance.

Coatings for aluminum should also comply with environmental requirements; therefore, a topical problem is the synthesis of lead-free enamels with the lowest possible temperature of coating firing.

Based on preliminary studies performed at the South-Russia State Technical University it was established that aluminophosphate enamel coatings meet the above requirements best of all [1].

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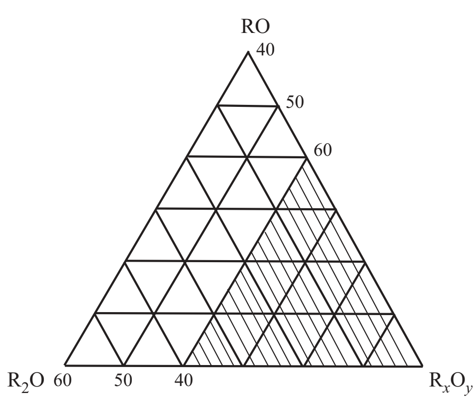

Fig. 1. Zone of formation of low-melting glasses in the $R_2O – RO – R_xO_y$ system [R_2O) $Li_2O + K_2O + Na_2O$; RO) $CuO + ZnO$; R_xO_y) $P_2O_5 + Al_2O_3 + B_2O_3 + TiO_2 + F^-$].

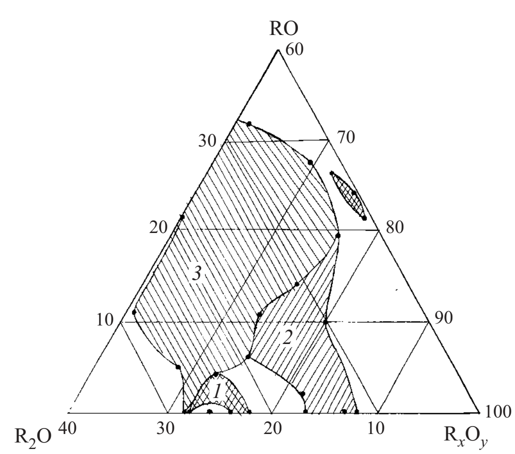

Fig. 2. Zones of formation of low-melting coatings for aluminum: *1*) coatings fusing at 570°C; *2*) coatings not fusing at 570°C; *3*) coatings not adhering to metal.

TABLE 1

Enamel	Mass content, %									
	P_2O_5	Al_2O_3	B_2O_3	TiO_2	CuO	ZnO	Li_2O	K_2O	Na_2O	F^-
1	32.70	24.66	11.20	6.50	–	–	–	3.50	19.70	1.64
2	69.54	6.93	2.07	–	9.52	10.84	1.14	–	–	–
3	44.00	21.20	7.10	–	4.00	–	3.70	–	20.00	–
4	48.20	21.70	–	2.40	–	–	–	9.20	18.50	–
5	68.45	2.78	1.91	–	15.37	9.58	1.91	–	–	–
6	72.25	2.24	1.54	–	12.00	10.06	1.32	–	–	–
7	38.00	21.26	6.00	5.00	–	–	–	4.00	18.00	1.64

We investigated specifics of glass formation in a multicomponent system of $R_2O – RO – Al_2O_3 – B_2O_3 – TiO_2 – P_2O_5$. The content of oxides in the range of glass formation varied within the following limits (here and elsewhere wt.%): 32 – 78 P_2O_5, 1 – 30 Al_2O_3, 0 – 12 B_2O_3, 0 – 8 TiO_2, 0 – 15 CuO, 0 – 15 ZnO, 0 – 10 Li_2O, 0 – 10 K_2O, 0 – 25 Na_2O, and 0 – 2 F^- (Fig. 1).

Frits were melted at 1100 – 1200°C in a Silit furnace with an exposure at a maximum temperature for 30 min and fritting in water.

In preparing enamel slip, 0.5% Veselovskoe clay and 0.5% $NaNO_2$ were added to frit. Aging of slip lasted 24 h.

The slip was applied to aluminum pretreated according to a method consisting of the following operations: degreasing aluminum plates with a solution (g/liter) of 50 Na_3PO_4 and 50 Na_2CO_3 at 60 – 70°C for 5 min; washing the plates in hot and cold distilled water; oxidation with a solution (g/liter) of 15 K_2CrO_4, 2.5 NaOH, and 50 Na_2CO_3 at a temperature of 85 – 95°C for 15 – 20 min; and finally, annealing at 550°C for 5 min.

The criteria accepted for the evaluation of technological properties of coatings were a firing temperature equal to 570°C and the degree of adhesion of a coating to metal. The zones of formation of a low-melting coating were constructed based on the results of firing and a fast evaluation (Fig. 2).

Coatings that fused at 570°C and were strongly fixed to the metal were selected for further studies. The compositions of these coatings are listed in Table 1.

The most significant properties of phosphor-bearing low-melting enamels include chemical resistance in aqueous solutions and acids and the strength of adhesion of a coating to aluminum. Chemical resistance was determined by Na_2O leaching in an aqueous medium, the mean adhesion index was found by the stepwise extraction method, and luster was determined with respect to the luster of UF 6 uviol glass (Table 2).

TABLE 2

Enamel	External appearance of coating		Luster, %	Adhesion strength, %	Chemical resistance, mg/cm^2 Na_2O
	degree of fusion at 570 ± 5°C, grades*	color			
1	5	Light lilac	65	72.15	0.192
2	3	Green	55	47.22	0
3	4	Emerald	64	69.17	0.047
4	4	Grayish-white	44	50.12	0.672
5	3	Olive	35	48.46	0
6	3	The same	34	49.99	0
7	4	Grayish-white	50	50.08	0.046

* The degree of fusion of coatings was evaluated in grades: 5) smooth, even surface without pinholes and bubbles; 4) smooth, even surface with a few pinholes; 3) surface with pinholes and bubbles; 2) non-fused rough surface; 1) non-sintered coating.

Based on the studies performed, it was found that enamel 1 has the optimum degree of adhesion to metal and luster. This enamel was accepted as a base variant and was analyzed using the thermographic and x-ray methods [2]. This particular enamel is a thin vitreous layer on metal surface. The strength of adhesion of enamel to aluminum is ensured by a transition layer formed at their contact boundary. X-ray phase analysis established that the transition layer contains the following crystalline phases: $Na_2O \cdot P_2O_5$, Al_2O_3, and $Al_2O_3 \cdot P_2O_5$ and besides P_2O_5 and Al_2O_3, which provide for high adhesion strength.

Formation of a high-quality coating depends on the content of P_2O_5 and Al_2O_3 in a glass matrix.

The restriction of the P_2O_5 content to 38% is due to deteriorated glass formation in the system (unmelted material is observed), and a higher content of this oxide impairs the chemical resistance (blisters arise on enamel surface in firing). The restriction of the Al_2O_3 content to 24% is due to a low firing temperature (up to 580°C) of coatings on aluminum and a relatively low melting temperature of phosphate glass matrixes.

In subsequent studies of the glass matrix, various additives decreasing the firing temperature were introduced in the composition (Na_2O, K_2O, and Li_2O) in the amount ranging from 1 to 5%. It was found that a 2% additive of Na_2O lowers the firing temperature by 20°C, and other additives, although decreasing the firing temperature, generate defects in the form of pinholes and bubbles.

The coloring oxides introduced into the glass matrix were NiO, Cr_2O_3, and Co_2O_3 in the amount up to 1%. It was found that a 0.5% additive of Co_2O_3 preserves an attractive

appearance of enamel, increases its firing temperature by 10°C, and imparts a uniformly saturated blue color to it. An increase in the content of the colorant oxides from 0.5 to 1% significantly increases the firing temperature and impairs the luster and external appearance of the coating.

Thus, the chemical resistance of the synthesized enamels is higher by an order of magnitude than that of earlier developed enamels. The firing temperature of the new enamels is lower by 50°C than that of earlier known similar enamels [3].

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